

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
3 January 2003 (03.01.2003)

PCT

(10) International Publication Number  
WO 03/001590 A2

(51) International Patent Classification<sup>7</sup>: H01L 21/768,  
21/285

95014 (US). CHUNG, Hua; 4645 Piper Drive, San Jose,  
CA 95129 (US). SINHA, Ashok; 4176 Hubbard Drive,  
Palo Alto, CA 94306 (US). KORI, Moris; 55 Hamilton  
Court, Palo Alto, CA 94301 (US).

(21) International Application Number: PCT/US02/19481

(74) Agents: PATTERSON, B. Todd et al.; MOSER, PAT-  
TERSON & SHERIDAN, L.L.P., 3040 Post Oak Blvd.,  
Suite 1500, Houston, TX 77056 (US).

(22) International Filing Date: 20 June 2002 (20.06.2002)

(81) Designated States (national): CN, JP, KR.

(25) Filing Language: English

(84) Designated States (regional): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE, TR).

(26) Publication Language: English

Published:

(30) Priority Data:  
09/885,609 20 June 2001 (20.06.2001) US

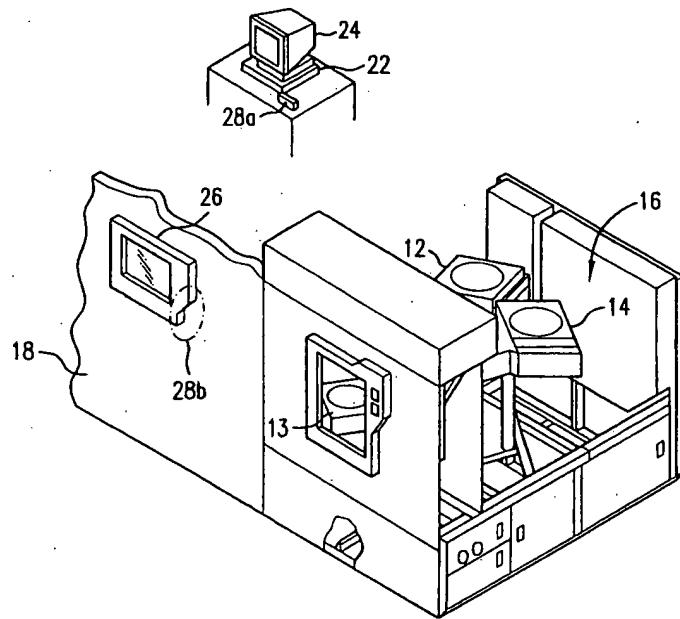
— without international search report and to be republished  
upon receipt of that report

(71) Applicant: APPLIED MATERIALS, INC. [US/US];  
3050 Bowers Avenue, Santa Clara, CA 95054 (US).

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(72) Inventors: MAK, Alfred W.; 32722 Fellows Court,  
Union City, CA 94587 (US). CHANG, Mei; 12881 Corte  
de Arguello, Saratoga, CA 95070 (US). BYUN, Jeong  
Soo; 20975 Valley Green Drive #257, Cupertino, CA

(54) Title: SYSTEM AND METHOD TO FORM A COMPOSITE FILM STACK UTILIZING SEQUENTIAL DEPOSITION  
TECHNIQUES



WO 03/001590 A2

(57) Abstract: A system and method to form a stacked barrier layer for copper contacts formed on a substrate. The substrate is serially exposed to first and second reactive gases to form an adhesion layer. Then, the adhesion layer is serially exposed to third and fourth reactive gases to form a barrier layer adjacent to the adhesion layer. This is followed by deposition of a copper layer adjacent to the barrier layer.

## SYSTEM AND METHOD TO FORM A COMPOSITE FILM STACK UTILIZING SEQUENTIAL DEPOSITION TECHNIQUES

### BACKGROUND OF THE INVENTION

5 This invention relates to the processing of semiconductor substrates. More particularly, this invention relates to improvements in the process of forming contacts.

Formation of contacts in multi-level integrated circuits poses many challenges to the semiconductor industry as the drive to increase circuit density continues, due to the reduction in size of the circuit features. Contacts are formed by depositing 10 conductive interconnect material in an opening on the surface of insulating material disposed between two spaced-apart conductive layers. The aspect ratio of such an opening inhibits deposition of conductive interconnect material that demonstrates satisfactory step coverage and gap-fill, employing traditional interconnect material such as aluminum. In addition, diffusion between the aluminum and the surrounding 15 insulating material often occurs, which adversely effects operation of the resulting electrical circuits.

20 Barrier materials have been introduced to improve both the step coverage and gap-fill of aluminum, while limiting diffusion of the same. Barrier materials must also provide good adhesion properties for aluminum. Otherwise, the thermal and electrical conductance of the resulting contact may be compromised. Examples of barrier materials providing the aforementioned characteristics include TiN, TiW, TiB<sub>2</sub>, TiC and Ti<sub>2</sub>N.

25 However, attempts have been made to provide interconnect material with lower electrical resistivity than aluminum. This has led to the substitution of copper aluminum. Copper, like aluminum, also suffers from diffusion characteristics and may form undesirable intermetallic alloys that reduce the availability of suitable barrier materials.

30 Tungsten has proved to be a suitable barrier material that effectively prevents diffusion of copper. Typically deposited employing chemical vapor deposition (CVD) techniques, tungsten deposition is attendant with several disadvantages. Tungsten diffuses easily into surrounding dielectric material. In addition, tungsten has proven difficult to deposit uniformly. This has been shown by variance in tungsten layers'

thickness of greater than 1%. As a result, it is difficult to control the resistivity of a tungsten layer.

What is needed, therefore, are improved techniques to form barrier layers for copper interconnects that include tungsten.

5

## SUMMARY OF THE INVENTION

One embodiment of the present invention is directed to a method to form a stacked barrier layer on a substrate disposed in a processing chamber by serially exposing the substrate to first and second reactive gases to form an adhesion layer. The adhesion 10 layer is then serially exposed to third and fourth reactive gases to form a barrier layer adjacent to the adhesion layer. A copper layer is disposed adjacent to the barrier layer. To that end, another embodiment of the invention is directed to a system to carry out the method.

## 15 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of a semiconductor processing system in accordance with the present invention;

Fig. 2 is a detailed view of the processing chambers shown above in Fig. 1;

Fig. 3 is a detailed cross-sectional view of a substrate shown above in Fig. 20 2 before deposition of a first refractory metal layer in accordance with one embodiment of the present invention;

Fig. 4 is a detailed cross-sectional view of the substrate shown above in Fig. 3 after deposition of a first refractory metal layer in accordance with one embodiment of the present invention;

25 Fig. 5 is a detailed cross-sectional view of a substrate shown above in Fig. 4 after deposition of a second refractory metal layer in accordance with one embodiment of the present invention;

Fig. 6 is a detailed cross-sectional view of a substrate shown above in Fig. 2 after deposition of a copper contact in accordance with one embodiment of the present 30 invention;

Fig. 7 is a schematic view showing deposition of a first molecule onto a substrate during sequential deposition techniques in accordance with one embodiment of the present invention;

5 Fig. 8 is a schematic view showing deposition of a second molecule onto a substrate during sequential deposition techniques in accordance with one embodiment of the present invention;

10 Fig. 9 is a graphical representation showing the concentration of gases introduced into the processing chamber shown above in Fig. 2, and the time in which the gases are present in the processing chamber to deposit the Titanium refractory metal layer shown above in Fig. 4, in accordance with one embodiment of the present invention; and

Fig. 10 is a graphical representation showing the concentration of gases introduced into the processing chamber shown above in Fig. 2, and the time in which the gases are present in the processing chamber to deposit the Tungsten layer shown above in Fig. 4, in accordance with one embodiment of the present invention.

## 15 DETAILED DESCRIPTION OF THE INVENTION

Referring to Fig. 1, an exemplary wafer processing system includes one or more processing chambers 12, 13 and 14 disposed in a common work area 16 surrounded by a wall 18. Processing chambers 12 and 14 are in data communication with a controller 22 that is connected to one or more monitors, shown as 24 and 26. Monitors 24 and 26 typically display common information concerning the process associated with the processing chambers 12 and 14. Monitor 26 is mounted to the wall 18, with monitor 24 being disposed in the work area 16. Operational control of processing chambers 12 and 14 may be achieved with use of a light pen, associated with one of monitors 24 and 26, to communicate with controller 22. For example, a light pen 28a is associated with monitor 24 and facilitates communication with the controller 22 through monitor 24. A light pen 28b facilitates communication with controller 22 through monitor 26.

Referring both to Figs. 1 and 2, each of processing chambers 12 and 14 includes a housing 30 having a base wall 32, a cover 34, disposed opposite to the base wall 32, and a sidewall 36, extending therebetween. Housing 30 defines a chamber 37,

and a pedestal 38 is disposed within processing chamber 37 to support a substrate 42, such as a semiconductor wafer. Pedestal 38 may be mounted to move between the cover 34 and base wall 32, using a displacement mechanism (not shown), but is typically fixed proximate to bottom wall 32. Supplies of processing gases 39a, 39b, 39c, 39d and 39e are 5 in fluid communication with the processing chamber 37 via a showerhead 40. Regulation of the flow of gases from supplies 39a, 39b and 39c is effectuated via flow valves 41.

Depending on the specific process, substrate 42 may be heated to a desired temperature prior to layer deposition via a heater embedded within pedestal 38. For example, pedestal 38 may be resistively heated by applying an electric current from an 10 AC power supply 43 to a heater element 44. Substrate 42 is, in turn, heated by pedestal 38, and can be maintained within a desired process temperature range of, for example, about 20 °C to about 750 °C, with the actual temperature varying dependent upon the gases employed and the topography of the surface upon which deposition is to occur. A 15 temperature sensor 46, such as a thermocouple, is also embedded in the wafer support pedestal 38 to monitor the temperature of the pedestal 38 in a conventional manner. For example, the measured temperature may be used in a feedback loop to control the electrical current applied to heater element 44 by the power supply 43, such that the wafer temperature can be maintained or controlled at a desired temperature that is suitable for the particular process application. Pedestal 38 is optionally heated using radiant heat (not 20 shown). A vacuum pump 48 is used to evacuate processing chamber 37 and to help maintain the proper gas flows and pressure inside processing chamber 37.

Referring to Figs. 1 and 3, one or both of processing chambers 12 and 14, discussed above, may operate to form, on substrate 42, a contact in accordance with the present invention on substrate 42. To that end, substrate 42 includes a wafer 50 that may 25 be formed from any material suitable for semiconductor processing, such as silicon. One or more layers, shown as layer 52, may be present on wafer 50. Layer 52 may be formed from any suitable material, including dielectric or conductive materials. Layer 52 includes a void 54, exposing a region 56 of substrate 42.

Referring to Fig. 4, formed adjacent to layer 52 and region 54 is a layer 30 containing a refractory metal compound, such as titanium. In the present example, layer 58 is formed from titanium nitride, TiN, by sequentially exposing substrate 42 to processing gases to chemisorb monolayers of differing compounds onto the substrate,

discussed more fully below. Layer 58 conforms to the profile of the void 54 so as to cover region 56 and layer 52.

Referring to Fig. 5, adjacent to layer 58 is formed an additional refractory metal layer 60. In the present example, layer 60 is formed from tungsten in the manner 5 discussed above with respect to layer 52, except using different process gases. Layer 60 conforms to the profile of layer 58 and, therefore, conforms to the profile of void 54.

Referring to Fig. 6, shown is one example of a contact 62 formed in void 54 in accordance with the present invention by deposition of a layer of copper 64 that fills void 54, using standard deposition techniques. With this configuration, a stacked barrier 10 layer consisting of TiN layer 58 and W layer 60 surrounds contact 62. TiN layer 58 serves as an adhesion layer to facilitate nucleation and deposition by W layer 60. TiN layer also serves as a diffusion barrier to reduce, if not prevent, diffusion of W into the surrounding environs, such as region 56 and layer 52. W layer 60 serves as a barrier layer for contact 62, thereby preventing copper material from diffusing into or through TiN 15 layer 58 and into the environs surrounding void 54. Employing sequential deposition techniques, such as atomic layer deposition, provides superior thermal and conductive characteristics of the aforementioned stacked barrier layer. Specifically, the sequential deposition techniques described below enable precise control over the thickness of both layers 58 and 60.

20 Referring to Figs. 1, 6 and 7, one or both of processing chambers 12 and 14, discussed above, may operate to deposit layers 58 and 60 on substrate 42 employing sequential deposition techniques. Specifically, the initial surface of substrate 42, e.g., the surface of region 56 and the surface of layer 52, presents an active ligand to the process region. A batch of a first processing gas, in this case  $Aa_x$ , results in a layer of A being 25 deposited on substrate 42 having a surface of ligand x exposed to the processing chamber 37. Thereafter, a purge gas enters processing chamber 37 to purge the gas  $Aa_x$ . After purging gas  $Aa_x$  from processing chamber 37, a second batch of processing gas,  $Bb_y$ , is introduced into processing chamber 37. The a ligand present on the substrate surface reacts with the b ligand and B atom, releasing molecules ab and Ba, that move away from 30 substrate 42 and are subsequently pumped from processing chamber 37. In this manner, a surface comprising a monolayer of A atoms remains upon substrate 42 and exposed to

processing chamber 37, shown in Fig. 4. The process proceeds cycle after cycle, until the desired thickness is achieved.

Referring to both Figs. 2 and 8, although any type of processing gas may be employed, in the present example, the processing gas  $Aa_x$  is a titanium-containing gas selected from the group that includes TDMAT, TDEAT and  $TiCl_4$ . The processing gas  $Bb_y$  functions as a reducing agent and is selected from the group including  $H_2$ ,  $B_2H_6$ ,  $SiH_4$  and  $NH_3$ . Two purge gases were employed:  $Ar$  and  $N_2$ . Each of the processing gases is flowed into processing chamber 37 with a carrier gas, which in this example, is one of the purge gases. It should be understood, however, that the purge gas may differ from the carrier gas, discussed more fully below. One cycle of the sequential deposition technique in accordance with the present invention includes flowing a purge gas into processing chamber 37 during time  $t_1$  before the titanium-containing gas is flowed into processing chamber 37. During time  $t_2$ , the titanium-containing processing gas is flowed into the processing chamber 37, along with a carrier gas. After  $t_2$  has lapsed, the flow of titanium-containing gas terminates and the flow of the carrier gas continues during time  $t_3$ , purging the processing chamber of the titanium-containing processing gas. During time  $t_4$ , the processing chamber 37 is pumped so as to remove all gases. After pumping of process chamber 37, a carrier gas is introduced during time  $t_5$ , after which time the reducing process gas is introduced into the processing chamber 37 along with the carrier gas, during time  $t_6$ . The flow of the reducing process gas into processing chamber 37 is subsequently terminated. After the flow of reducing process gas into processing chamber 37 terminates, the flow of carrier gas continues, during time  $t_7$ . Thereafter, processing chamber 37 is pumped so as to remove all gases therein, during time  $t_8$ , thereby concluding one cycle of the sequential deposition technique in accordance with the present invention. The aforementioned cycle is repeated multiple times until layer 58 reaches a desired thickness. After TiN layer 58 reaches a desired thickness, W layer 60 is deposited adjacent thereto employing sequential deposition techniques.

Referring to Figs. 2 and 10, to form W layer 60, processing gas  $Aa_x$  may be any known tungsten-containing gas, such as tungsten hexafluoride,  $WF_6$ . The processing gas  $Bb_y$  functions as a reducing agent and is selected from the group including  $SiH_4$ ,  $B_2H_6$  and  $NH_3$ . The same purge gases may be employed, as discussed above. Each of the processing gases is flowed into the processing chamber 37 with a carrier gas, as

discussed above. One cycle of the sequential deposition technique to form W layer 60 in accordance with the present invention includes flowing a purge gas into the processing chamber 37 during time  $t_9$ , before the tungsten-containing gas is flowed into the processing chamber 37. During time  $t_{10}$ , the tungsten-containing processing gas is flowed 5 into the processing chamber 37, along with a carrier gas. After time  $t_{10}$  has lapsed, the flow of tungsten-containing gas terminates and the flow of the carrier gas continues during time  $t_{11}$ , purging the processing chamber of the tungsten-containing processing gas. During time  $t_{12}$ , processing chamber 37 is pumped so as to remove all gases. After pumping of the process chamber 37, a carrier gas is introduced during time  $t_{13}$ , after 10 which time the reducing process gas is introduced into the processing chamber 37 along with the carrier gas, during time  $t_{14}$ . The flow of the reducing process gas into processing chamber 37 is subsequently terminated. After the flow of reducing process gas into the processing chamber 37 terminates, the flow of carrier continues during time  $t_{15}$ . Thereafter, the processing chamber 37 is pumped so as to remove all gases therein, during 15 time  $t_{16}$ , thereby concluding one cycle of the sequential deposition technique in accordance with the present invention. The aforementioned cycle is repeated multiple times until layer 60 reaches a desired thickness. After W layer 60 reaches a desired thickness, the contact 62, shown in Fig. 6 may be deposited employing known techniques.

The benefits of employing sequential deposition are manifold, including 20 flux-independence of layer formation that provides uniformity of deposition independent of the size of a substrate. For example, the measured difference of the layer uniformity and thickness measured between a 200 mm substrate and a 32 mm substrate deposited in the same chamber is negligible. This is due to the self-limiting characteristics of chemisorption. Further, the chemisorption characteristics contribute to near-perfect step 25 coverage over complex topography.

In addition, the thickness of the layers 58 and 60 may be easily controlled while minimizing the resistance of the same by employing sequential deposition techniques. In one example of the present invention, layers 58 and 60, as well as contact 30 62 may be deposited in a common processing chamber, for example chambers 12 and 14. To provide added flexibility when depositing layers 58 and 60, as well as contact 62, a bifurcated deposition process may be practiced in which layer 58 is deposited in one process chamber, for example chamber 12, and layer 60 is deposited in a separate

10. The method as recited in claim 1 wherein said first reactive gas is selected from the group consisting essentially of TDMAT, TDEAT and  $TiCl_4$  and said second reactive gas is selected from the group consisting essentially of  $H_2$ ,  $B_2H_6$ ,  $SiH_4$  and  $NH_3$ .

5 11. The method as recited in claim 1 wherein said third reactive gas is  $WF_6$  and said fourth reactive gas is selected from the group consisting essentially of  $SiH_4$ ,  $B_2H_6$  and  $NH_3$ .

10 12. The method as recited in claim 1 wherein serially exposing said substrate further includes serially introducing said first reactive gas and said second reactive gas into said processing chamber, and purging said processing chamber of said first reactive gas before introducing said second reactive gas by introducing a purge gas into said processing chamber after exposing said substrate to said first reactive gas and before exposing said substrate to said second reactive gas.

15 13. The method as recited in claim 1 wherein serially exposing said substrate further includes serially introducing said first reactive gas and said second reactive gas into said processing chamber, and purging said processing chamber of said first reactive gas before introducing said second reactive gas by pumping said processing chamber clear of said first reactive gas before introducing said second reactive gas.

20 14. The method as recited in claim 1 wherein serially exposing said adhesion layer further includes serially introducing said third and fourth reactive gases into said processing chamber, and purging said processing chamber of said third reactive gas before introducing said fourth reactive gas by introducing a purge gas into said processing chamber after exposing said substrate to said third reactive gas and before exposing said substrate to said fourth reactive gas.

25 15. The method as recited in claim 1 wherein serially exposing said adhesion layer further includes serially introducing said third and fourth reactive gases into said processing chamber, and purging said processing chamber of said third reactive gas before introducing said fourth reactive gas by pumping said processing chamber clear of said third reactive gas before introducing said fourth reactive gas.



chamber, for example chamber 14. This may reduce the deposition time of each of layers 58 and 60 by, *inter alia*, having each processing chamber 12 and 14 preset to carry-out the process parameters necessary to deposit the requisite refractory metal layers.

Referring again to Fig. 2, the process for depositing the tungsten layer may 5 be controlled using a computer program product that is executed by the controller 22. To that end, the controller 22 includes a central processing unit (CPU) 70, a volatile memory, such as a random access memory (RAM) 72 and permanent storage media, such as a floppy disk drive for use with a floppy diskette, or hard disk drive 74. The computer program code can be written in any conventional computer readable programming 10 language; for example, 68000 assembly language, C, C++, Pascal, Fortran, and the like. Suitable program code is entered into a single file, or multiple files, using a conventional text editor and stored or embodied in a computer-readable medium, such as the hard disk drive 74. If the entered code text is in a high level language, the code is compiled and the resultant compiler code is then linked with an object code of precompiled Windows® 15 library routines. To execute the linked and compiled object code the system user invokes the object code, causing the CPU 70 to load the code in RAM 72. The CPU 70 then reads and executes the code to perform the tasks identified in the program.

Although the invention has been described in terms of specific 20 embodiments, one skilled in the art will recognize that various changes to the reaction conditions, i.e., temperature, pressure, film thickness and the like can be substituted and are meant to be included herein and sequence of gases being deposited. For example, sequential deposition process may have a different initial sequence. The initial sequence 25 may include exposing the substrate to the reducing gas before the metal-containing gas is introduced into the processing chamber. In addition, other stacked layers may be deposited, in addition to the refractory-metal layers described above and for purposes other than formation of a barrier layer. Tungsten and other deposition techniques may be employed in lieu of CVD. For example, physical vapor deposition (PVD) techniques, or a combination of both CVD and PVD techniques, may be employed. Therefore, the scope of the invention should not be based upon the foregoing description. Rather, the 30 scope of the invention should be determined based upon the claims recited herein, including the full scope of equivalents thereof.

## WHAT IS CLAIMED IS:

1. A method for forming a stacked barrier layer on a substrate disposed in a processing chamber, said method comprising:
  - 5 serially exposing said substrate to first and second reactive gases to form an adhesion layer; and
  - serially exposing said adhesion layer to third and fourth reactive gases to form a barrier layer adjacent to said adhesion layer.
- 10 2. The method as recited in claim 1 further including depositing a layer of copper adjacent to said barrier layer.
- 15 3. The method as recited in claim 1 further including repeating serially exposing said substrate to first and second reactive gases to form said adhesion layer to a desired thickness before serially exposing said adhesion layer to third and fourth reactive gases.
4. The method as recited in claim 3 further including repeating serially exposing said substrate to third and fourth reactive gases to form said barrier layer to a desired thickness after serially exposing said substrate to first and second reactive gases.
- 20 5. The method as recited in claim 1 further including providing first and second processing chambers wherein serially exposing said substrate to first and second reactive gases further includes serially exposing said substrate to said first and second reactive gases while said substrate is disposed in said first processing chamber and serially exposing said adhesion layer to third and fourth reactive gases further includes serially exposing said adhesion layer to third and fourth reactive gases while said substrate is positioned in said second processing chamber.
- 25

6. The method as recited in claim 3 further including providing first and second processing chambers wherein serially exposing said substrate to first and second reactive gases further includes serially exposing said substrate to said first and second reactive gases while said substrate is disposed in said first processing chamber and serially exposing said adhesion layer to third and fourth reactive gases further includes serially exposing said adhesion layer to third and fourth reactive gases while said substrate is positioned in said first processing chamber and depositing a layer of copper adjacent to said barrier layer further includes depositing a copper layer adjacent to said barrier layer when said substrate is positioned in said second processing chamber.

10 7. The method as recited in claim 3 further including providing first, second and third processing chambers wherein serially exposing said substrate to first and second reactive gases further includes serially exposing said substrate to said first and second reactive gases while said substrate is disposed in said first processing chamber and serially exposing said adhesion layer to third and fourth reactive gases further includes 15 serially exposing said adhesion layer to third and fourth reactive gases while said substrate is positioned in said first processing chamber and depositing a layer of copper adjacent to said barrier layer further includes depositing a copper layer adjacent to said barrier layer when said substrate is positioned in said third processing chamber.

20 8. The method as recited in claim 1 wherein serially exposing said substrate further includes introducing said second reactive gas into said processing chamber and further including purging said processing chamber of said second reactive gas before exposing said adhesion layer to said third reactive gas.

25 9. The method as recited in claim 1 wherein said first and third gases each includes a refractory metal compound, with the refractory metal compound associated with said first reactive gas differing from the refractory metal compound associated with said third reactive gas.

10. The method as recited in claim 1 wherein said first reactive gas is selected from the group consisting essentially of TDMAT, TDEAT and  $TiCl_4$  and said second reactive gas is selected from the group consisting essentially of  $H_2$ ,  $B_2H_6$ ,  $SiH_4$  and  $NH_3$ .

5 11. The method as recited in claim 1 wherein said third reactive gas is  $WF_6$  and said fourth reactive gas is selected from the group consisting essentially of  $SiH_4$ ,  $B_2H_6$  and  $NH_3$ .

10 12. The method as recited in claim 1 wherein serially exposing said substrate further includes serially introducing said first reactive gas and said second reactive gas into said processing chamber, and purging said processing chamber of said first reactive gas before introducing said second reactive gas by introducing a purge gas into said processing chamber after exposing said substrate to said first reactive gas and before exposing said substrate to said second reactive gas.

15 13. The method as recited in claim 1 wherein serially exposing said substrate further includes serially introducing said first reactive gas and said second reactive gas into said processing chamber, and purging said processing chamber of said first reactive gas before introducing said second reactive gas by pumping said processing chamber clear of said first reactive gas before introducing said second reactive gas.

20 14. The method as recited in claim 1 wherein serially exposing said adhesion layer further includes serially introducing said third and fourth reactive gases into said processing chamber, and purging said processing chamber of said third reactive gas before introducing said fourth reactive gas by introducing a purge gas into said processing chamber after exposing said substrate to said third reactive gas and before exposing said substrate to said fourth reactive gas.

25 15. The method as recited in claim 1 wherein serially exposing said adhesion layer further includes serially introducing said third and fourth reactive gases into said processing chamber, and purging said processing chamber of said third reactive gas before introducing said fourth reactive gas by pumping said processing chamber clear of said third reactive gas before introducing said fourth reactive gas.

16. A method for forming a stacked barrier layer on a substrate disposed in a processing chamber, said method comprising:

serially exposing said substrate to first and second reactive gases to form an adhesion layer, by introducing said first reactive gas into said processing chamber and  
5 removing said first reactive gas from said processing chamber before introducing said second reactive gas;

repeating serially exposing said substrate to first and second reactive gases to form said adhesion layer to a desired thickness;

10 serially exposing said adhesion layer to third and fourth reactive gases to form a barrier layer adjacent to said adhesion layer by introducing said third reactive gas into said processing chamber and clearing said third reactive gas from said processing chamber before introducing said fourth reactive gas;

repeating serially exposing said substrate to third and fourth reactive gases to form said barrier layer to an acceptable thickness;

15 purging said processing chamber of said first and second reactive gases before introducing either of said third and fourth reactive gases; and  
depositing a layer of copper adjacent to said barrier layer.

17. The method as recited in claim 16 wherein said first reactive gas being selected from the group consisting essentially of TDMAT, TDEAT and  $TiCl_4$ , said  
20 second reactive gas being selected from the group consisting essentially of  $H_2$ ,  $B_2H_6$ ,  $SiH_4$  and  $NH_3$ , said third reactive gas being  $WF_6$ , and said fourth reactive gas being selected from the group consisting essentially of  $SiH_4$ ,  $B_2H_6$  and  $NH_3$ .

18. The method as recited in claim 16 wherein serially exposing said substrate to first and second reactive gases further includes removing said first reactive gas from said processing chamber before introducing said second reactive gas by introducing an inert gas into said processing chamber, and serially exposing said adhesion layer to third and fourth reactive gases further includes clearing said third reactive gas from said processing chamber before introducing said fourth reactive gas by introducing an expulsion gas into said processing chamber, and purging said processing chamber of said first and second reactive gases further includes purging said processing chamber by introducing a purge gas into said processing chamber.

10 19. The method as recited in claim 16 wherein serially exposing said substrate to first and second reactive gases further includes removing said first reactive gas from said processing chamber before introducing said second reactive gas by pumping said processing chamber clear of said first reactive gas, and serially exposing said adhesion layer to third and fourth reactive gases further includes clearing said third reactive gas from said processing chamber by pumping said processing chamber clear of said third reactive gas, and purging said processing chamber of said first and second reactive gases further includes pumping said processing chamber clear of all gases present therein.

15

20. A processing system for forming a stacked barrier layer on a substrate in a processing chamber, said system comprising:

means, coupled to said processing chamber, for serially exposing said substrate to first and second reactive gases to form an adhesion layer, by introducing said 5 first reactive gas into said processing chamber and removing said first reactive gas from said processing chamber before introducing said second reactive gas;

means, coupled to said processing chamber, for repeating serially exposing said substrate to first and second reactive gases to form said adhesion layer to a desired thickness;

10 means, coupled to said processing chamber, for serially exposing said adhesion layer to third and fourth reactive gases to form a barrier layer adjacent to said adhesion layer by introducing said third reactive gas into said processing chamber and clearing said third reactive gas from said processing chamber before introducing said fourth reactive gas;

15 means, coupled to said processing chamber, for repeating serially exposing said substrate to third and fourth reactive gases to form said adhesion layer to a desired thickness before serially exposing said adhesion layer to third and fourth reactive gases;

means, coupled to said processing chamber, for purging said processing chamber of said first and second reactive gases before introducing either of said third and 20 fourth reactive gases; and

means, coupled to said processing chamber, for depositing a layer of copper adjacent to said barrier layer.

21. A processing system for forming a stacked barrier layer on a substrate, said system comprising:

- a body defining a processing chamber;
- a holder disposed within said processing chamber to support said substrate;
- 5 a gas delivery system in fluid communication with said processing chamber;
- a first temperature control system in thermal communication with said processing chamber;
- 10 a pressure control system in fluid communication with said processing chamber;
- a controller in electrical communication with said gas delivery system, said temperature control system, and said pressure control system; and
- 15 a memory in data communication with said controller, said memory comprising a computer-readable medium having a computer-readable program embodied therein, said computer-readable program including a first set of instructions for controlling said gas delivery system to serially exposing said substrate to first and second reactive gases to form an adhesion layer on said substrate, and a second set of instructions to control said gas delivery system to serially expose said adhesion layer to third and fourth reactive gases to form a barrier layer adjacent to said adhesion layer.

20 22. The system as recited in claim 21 wherein said computer-readable program includes a third set of instructions to control said gas delivery system to remove said first reactive gas from said processing chamber before introducing said second reactive gas by introducing an inert gas into said processing chamber, and a fourth set of instructions to control said gas delivery system to clear said third reactive gas from said 25 processing chamber before introducing said fourth reactive gas by introducing an expulsion gas into said processing chamber, and a fifth set of instructions to control said gas delivery system to purge said processing chamber of said first and second reactive gases before introducing said third and fourth reactive gases by introducing a purge gas into said processing chamber.

23. The system as recited in claim 21 wherein said computer-readable program includes a third set of instructions to control said pressure control system to remove said first reactive gas from said processing chamber before introducing said second reactive gas by pumping said processing chamber clear of said first reactive gas, a 5 fourth set of instructions to control said pressure control system to and clear said third reactive gas from said processing chamber before introducing said fourth reactive gas by pumping said processing chamber clear of said third reactive gas, and a fifth set of instructions to control said pressure control system to purge said processing chamber of said first and second reactive gases before introducing said third and fourth reactive gases 10 by pumping said processing chamber clear of said first and second reactive gases.

24. The system as recited in claim 23 wherein serially exposing said substrate includes serially exposing said substrate to first and second reactive gases to form a titanium-containing adhesion layer, and serially exposing said adhesion layer to third and fourth reactive gases to form a tungsten-containing barrier layer adjacent to said 15 titanium-containing adhesion layer.

25. The system as recited in claim 23 wherein said first reactive gas is selected from the group consisting essentially of TDMAT, TDEAT and  $TiCl_4$ , said second reactive gas is selected from the group consisting essentially of  $H_2$ ,  $B_2H_6$  and  $SiH_4$ , said third reactive gas is  $WF_6$ , and said fourth reactive gas is selected from the 20 group consisting essentially of  $SiH_4$ ,  $B_2H_6$  and  $NH_3$ .

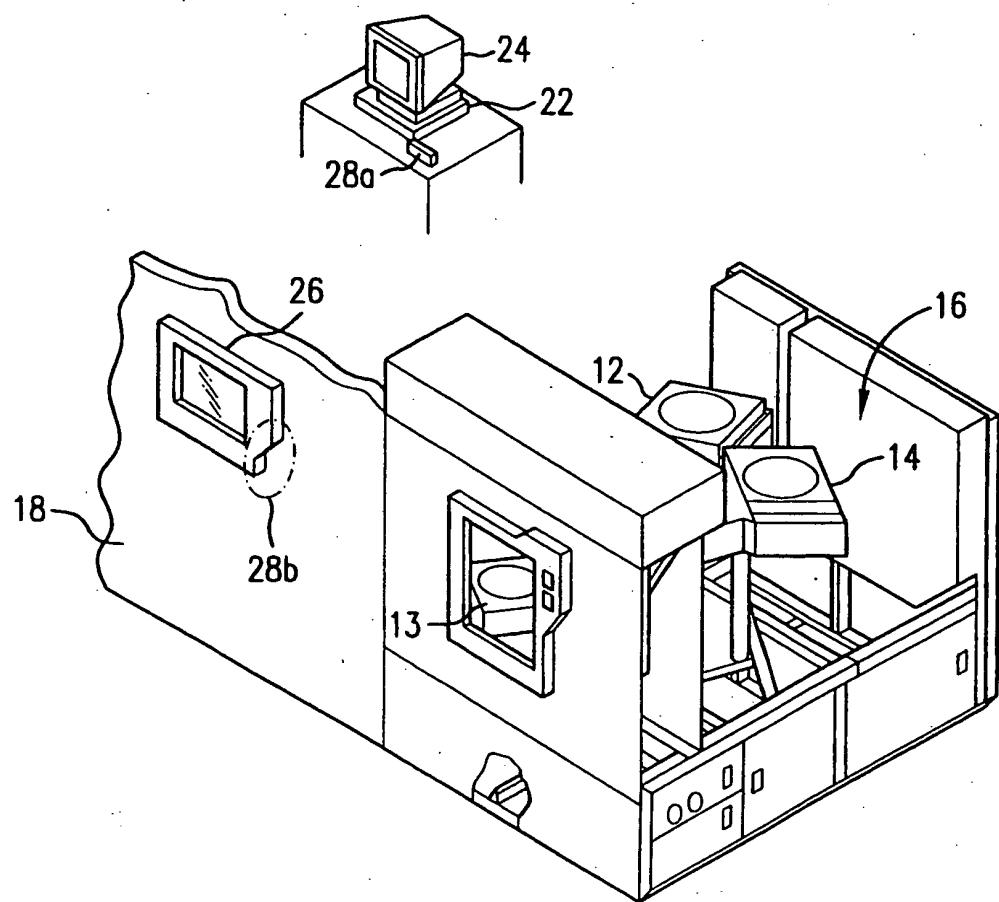
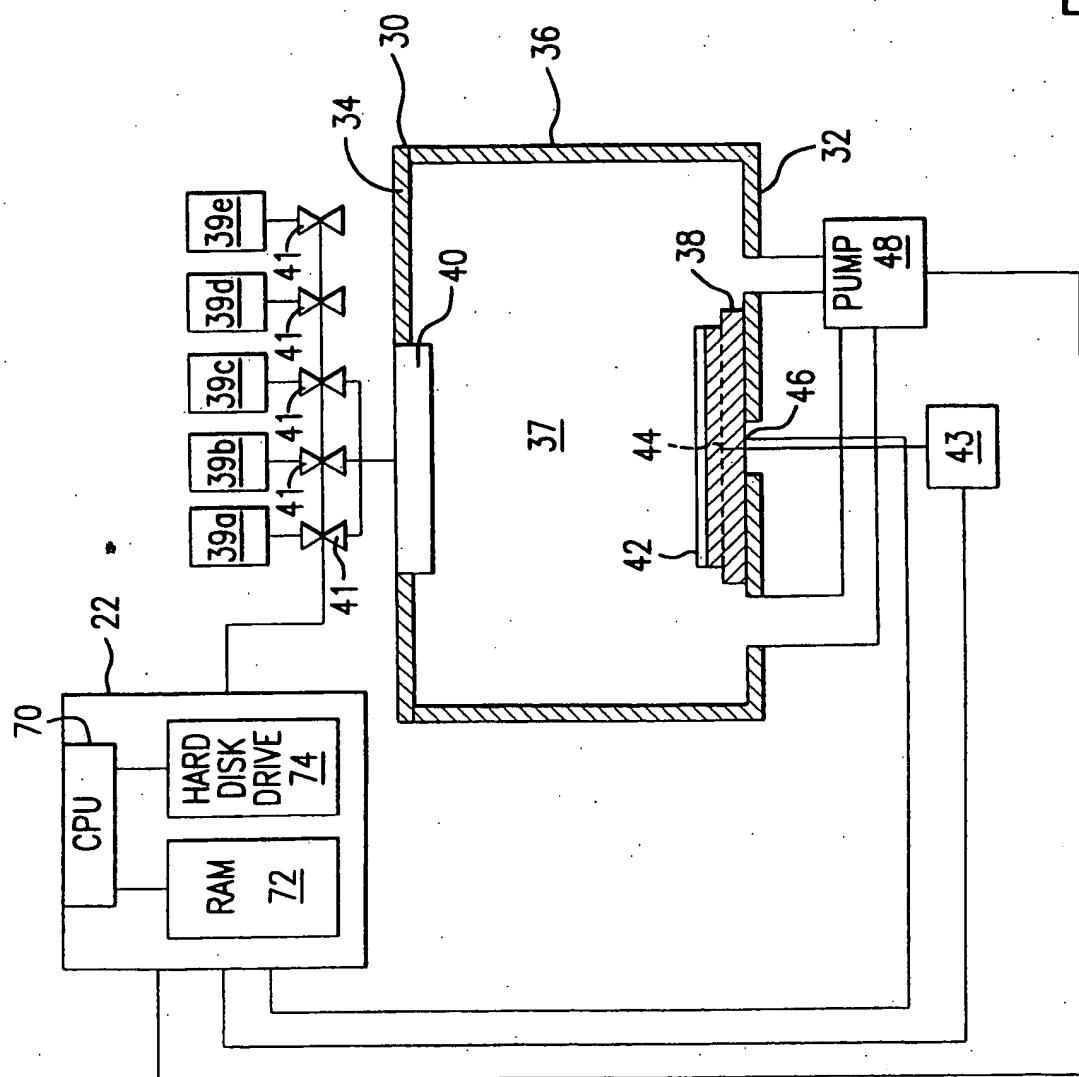


FIG. 1

FIG. 2



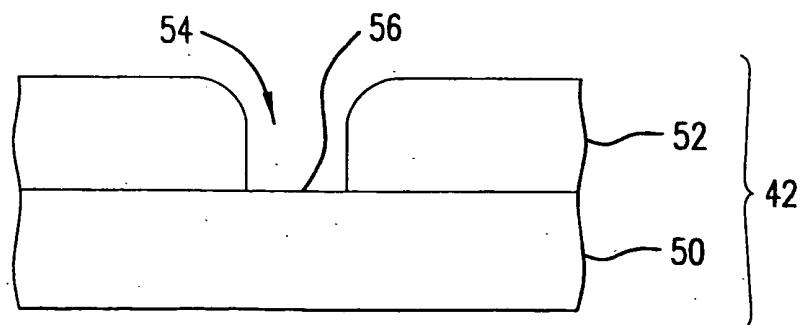


FIG. 3

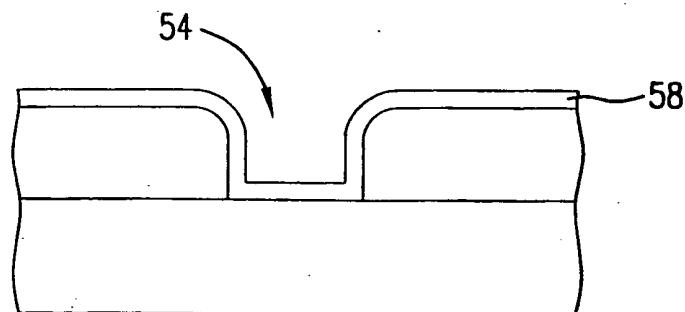


FIG. 4

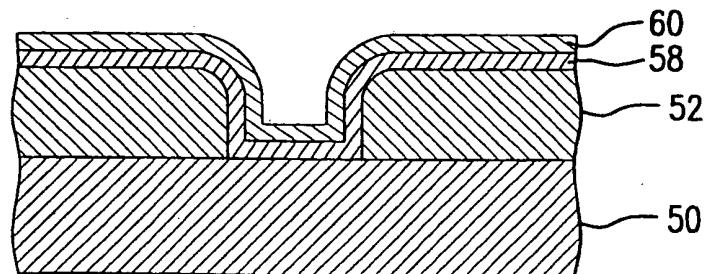


FIG. 5

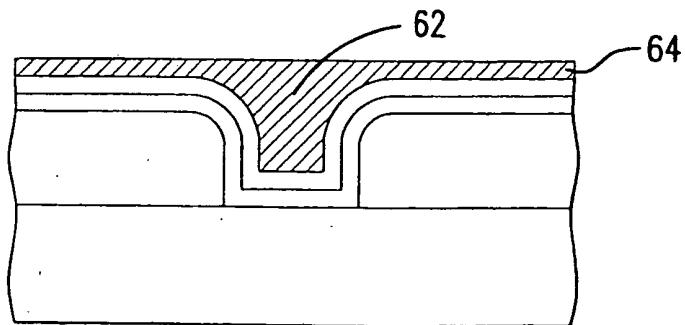


FIG. 6

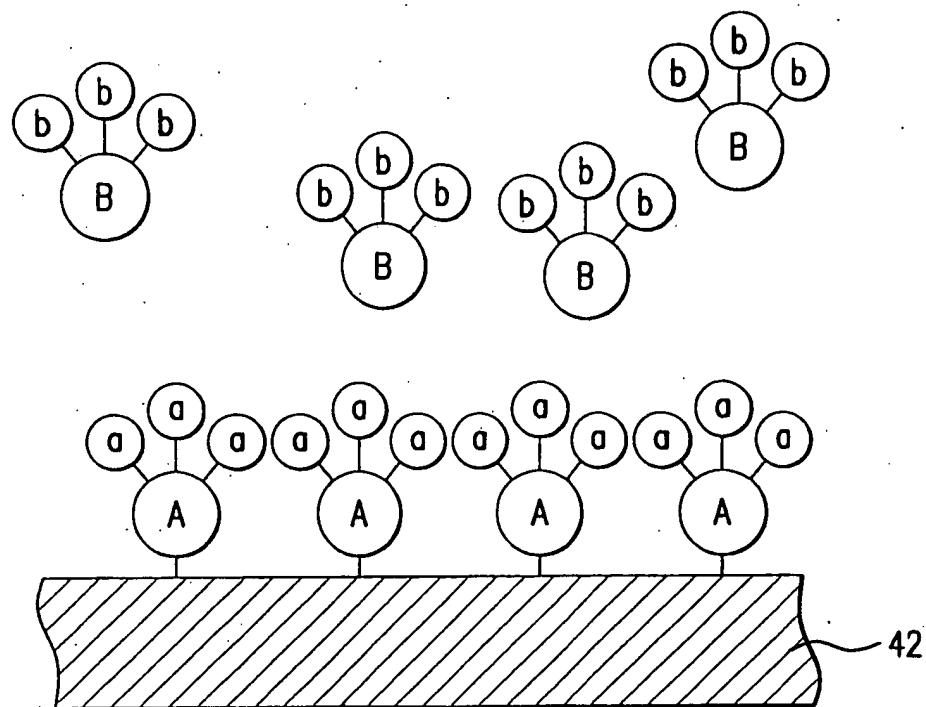


FIG. 7

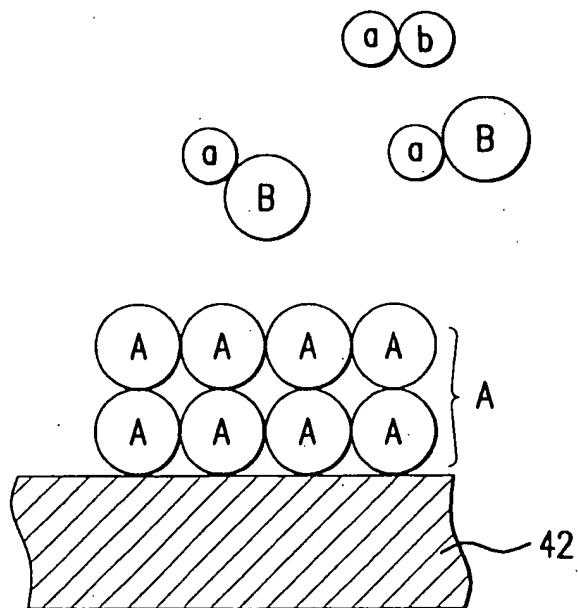


FIG. 8

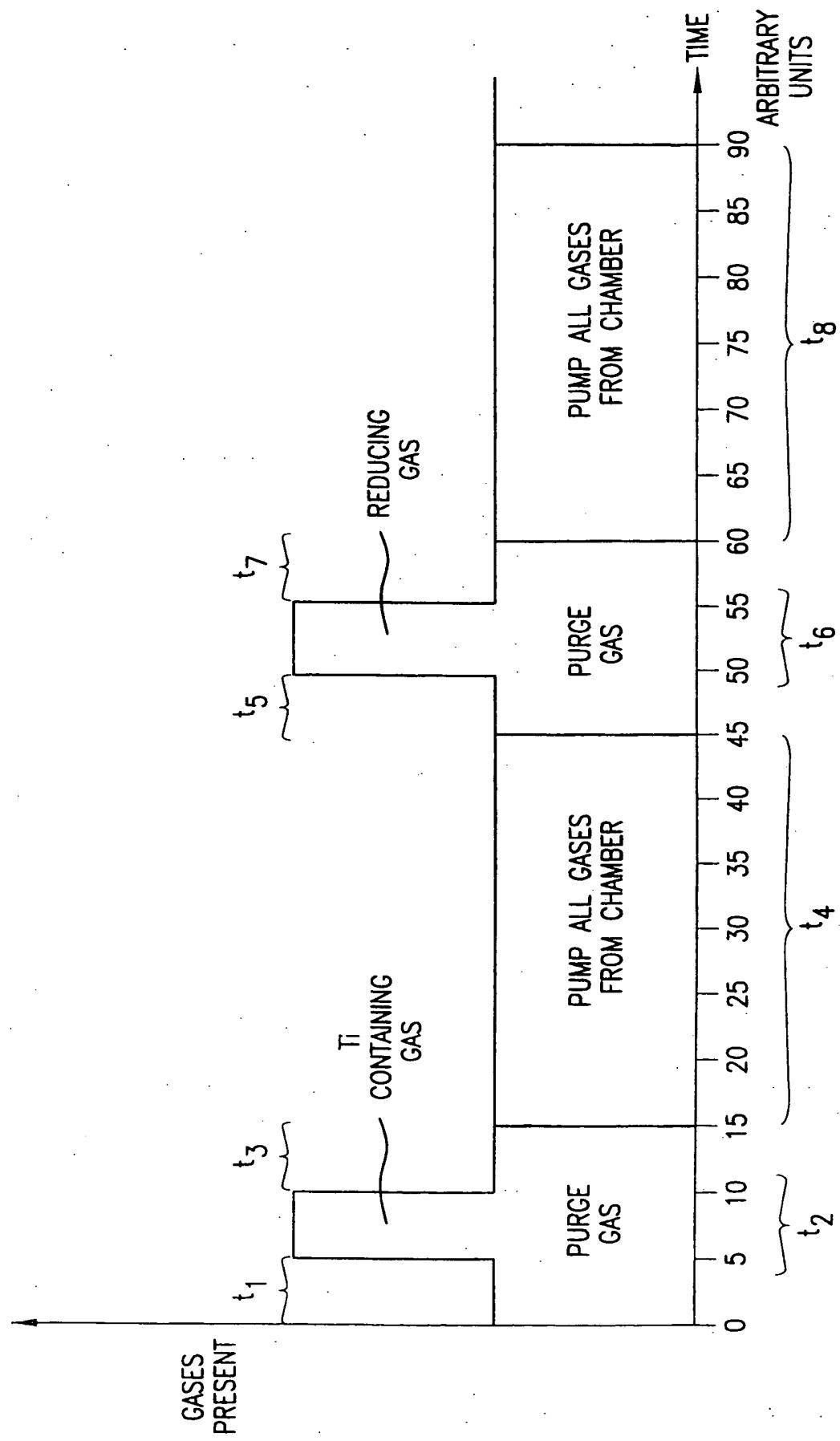


FIG. 9

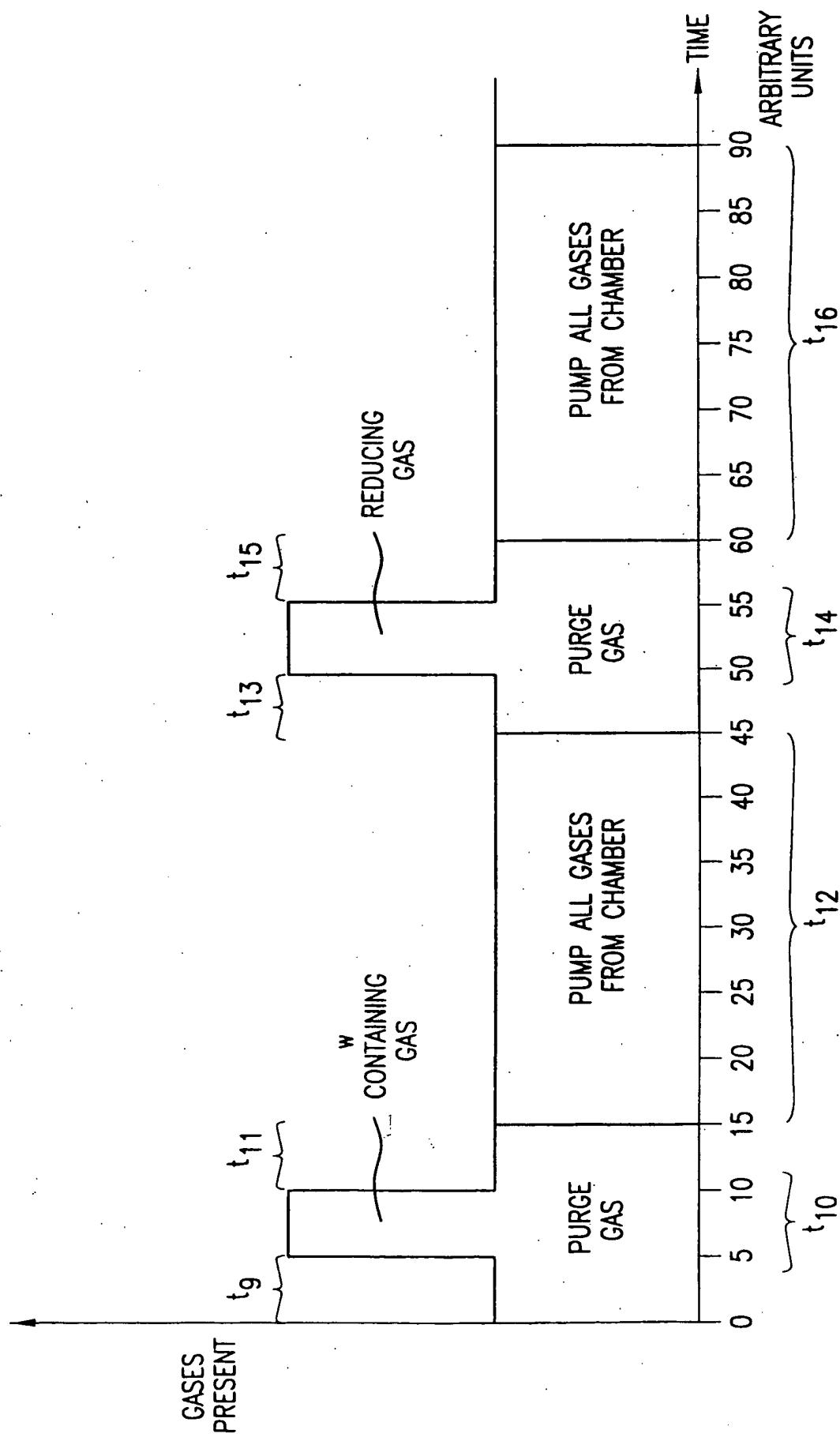


FIG. 10

